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Design and Performance of a Miniature Dual-Beam Diode-Array Spectrometer

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A miniature dual-beam diode-array spectrometer has been developed that operates in four spectral regions from the ultraviolet to the near-infrared. Two spectra, representing the sample and a reference, are dispersed onto a single diode array with a single grating. Measurements of spectral bandwidth, stray light, and sensitivity are described. Examples of Instrument operation in the transmission and reflectance modes are presented. The small size of the instrument makes it convenient for on-line or field measurements.

iode-array spectrometers have become increasingly popular in recent years, largely because of their ability to acquire multiwavelength data very rapidly using no moving parts. Most commercially available diode-array spectrometers are single beam, although many spectroscopic measurements are dual beam in nature. Examples include transmission and reflectance measurements. or when spectral features of the sample need to be monitored in real-time relative to a reference material. With a single-beam instrument, one must be concerned with light-source variations occurring between measurements. which is much less of a concern when a dual-beam instrument is used.

This article describes the optical design and performance of a miniature dual-beam diode-array spectrometer having moderate (~10 nm) spectral resolution and presents examples of transmission and reflectance spectra. Using a novel optical design, a single concave holographic grating disperses light from two slits along a 12.8-mm photodiode array. Two spectra — sample and reference — are thus measured simultaneously. The spectrometer focal distance is 60.8 mm and the f number is $f/2$. The spectrometer detector, a 256-element photodiode array, includes a 16-bit analog-to-digital (A/D) converter and communications interface to a personal computer. Data can be stored in ASCII file format for subsequent processing. The dimensions of the optical module with A/D converter are 6.5 cm H × 6.5 cm W × 14 cm L. Four gratings are available, providing spectral coverage from the ultraviolet (UV) to the near-infrared (near-IR). The spectrometer consists of the MDS optical module and the diode-array detector with associated electronics.

OPTICAL MODULE

The MDS optical module is cylindrical, with the grating at one end and the two slits and detector at the opposite end. Figure 1 shows a side view of the module. Light enters the two slits and then passes through glass filters located behind the slits. The purpose of these filters is explained below. After passing through the filters, the light strikes the grating and is dispersed and focused onto the diode array.
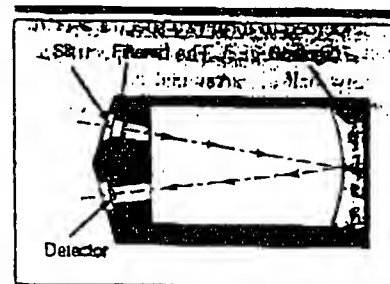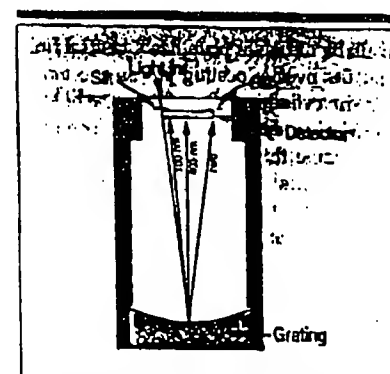

Figure 1. Side view of the MD5 optical module.

Figure 2. MD5 optical schematic showing wavelength distribution over the diode array.

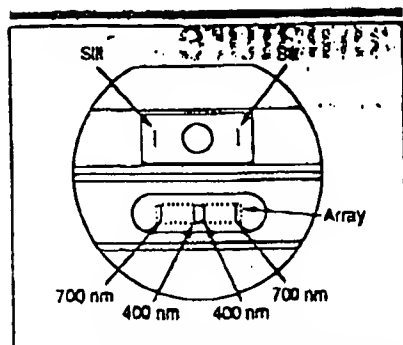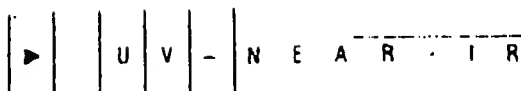Figure 3. Slit and detector view of the MDS optical module.

Figure 4. Spectrum of a low-pressure mercury lamp obtained with the MDS color spectrometer.

Figure 2 is a schematic diagram showing the dispersion of light from one of the slits. In this figure, the positive first-order spectrum from the left slit is dispersed over the array. The zero-order light (undispersed) is imaged off the array. Light of wavelengths shorter than 400 nm (for the "color" version of the module) is absorbed by the glass filter located behind the slit. Light entering the other slit is dispersed in the opposite direction along the array, and a second filter behind this slit absorbs the shorter wavelengths. Therefore, white light entering both slits is dispersed to form two spectra over the 400-700-nm region. The two spectra each occupy half the array and have opposite dispersion. Figure 3 is a schematic diagram of the slit and detector end of the module showing the location of the two spectra with respect to the array. The unused negative first-order and higher-order light strikes the spectrometer wall, which is covered with a strongly absorbing black material.

The standard spectrometer slit plate has two 100-μm × 2.5-mm slits; slit dimensions of 100 μm × 1.0 mm, 50 μm × 1.0 mm, and 50 μm × 2.5 mm are also available. The slit plate has a central hole that fits over a locating pin on the body, and the cylindrical glass filters are held in the MDS body by the slit plate. The optical module thus consists of three optical components: the grating, which is cemented into the body, and two glass filters. There are no moving parts and no adjustments, except for initial positioning of the detector.

The spectrum of a low-pressure mercury lamp obtained with the color version of the MDS is shown in Figure 4. Note the approximate mirror symmetry about the array center: the symmetry is not perfect because the intensity of the light
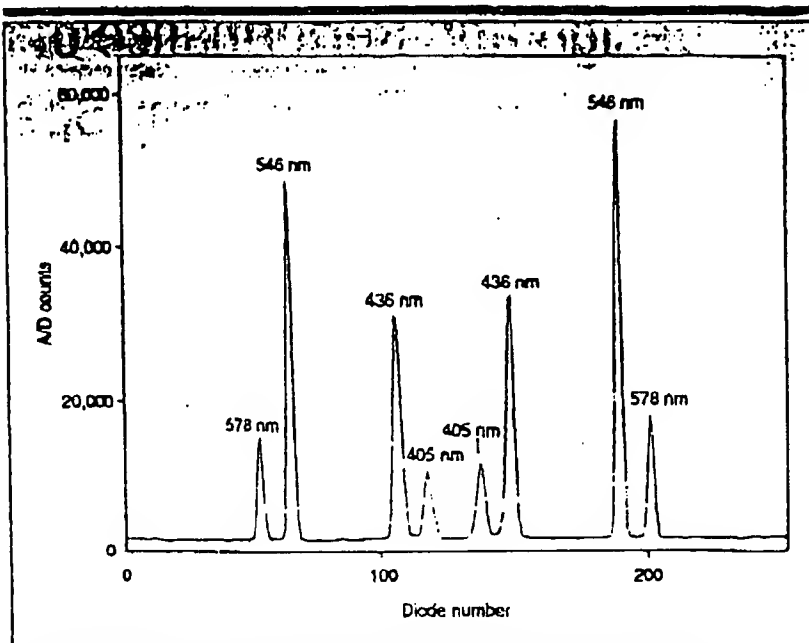
entering the slits is generally not equal, and small differences in grating illumination may exist between the two paths.

DETECTOR AND ELECTRONICS

The main restriction on the choice of detector is that its overall length is about 13 mm (or less), since the slit separation is 13.8 mm. Thus, 256-element silicon photodiode arrays having diodes on 50-μm centers, or 512-element arrays with diodes on 25-μm centers, can be used. Examples are the EG&G (Sunnyvale, CA) types RL0256TB and RL0512SB and Hamamatsu (Hamamatsu City, Japan) types S3921-256Q and S3924-512Q. We presently use an EG&G RL0256TBU detector, which has 256 elements on 50-μm centers. The array is used without a cover plate to reduce stray light resulting from internal reflections within the plate; transmission in the short wavelength UV is also improved. The detector socket is mounted on a small circuit board with two holes on either side. Two screws hold the detector board to the MDS body. The mounting holes are slightly oversize to permit some lateral adjustment (centering) of the detector.

The EG&G detector is interfaced to an A/D converter (16 bit, 10 MHz), which mounts on top of the MDS module. The A/D board microprocessor communicates with a host interface box (HIB),

which communicates with an IBM-compatible personal computer. Evaluation software, written in C, enables the user to quickly obtain data at different integration times and formats. The data can be saved to ASCII files and exported into other programs for further processing. For example, we use LabCalc software (Galactic Industries, Salem, NH) for spectral analysis.

WAVELENGTH CALIBRATION

The demonstration software includes a program for wavelength calibration using linear regression (least squares) analysis. An analysis of the wavelength distribution using the grating equation shows that assuming a linear relationship between diode position and wavelength results in a maximum error of ~2 nm over the 380-730-nm wavelength range. Additional errors, of course, arise from the uncertainty in the slopes and intercepts derived using linear regression. An analysis of these errors suggests that, if the diode positions are determined to ±0.1 pixel, the uncertainty in the wavelengths obtained from linear regression on four calibration lines is 1-2 nm. This is of the same magnitude as the departure of the calibration curve from linearity. Therefore, it appears that even if more calibration lines were used, the accuracy would be no better than about ±1 nm. Better ac-

curacy should be possible using a polyno-
mial with quadratic or cubic terms or
both.

We typically use low-pressure mercury
or argon lines for calibration. Light from
these lamps is coupled to the spectrome-
ter slits using glass or optical quartz fiber
optics. Wavelengths that have been found
useful for MD5 calibration are given in
Table I.

SPECTRAL LINE WIDTH MEASUREMENTS

The usual definition of spectral resolution
is given by the Rayleigh criterion. Accord-
ing to this criterion, two lines of equal in-
tensity are resolved if there is valley of
~20% between the two peaks (1). In prac-
tice, however, it is difficult to find spectral
line pairs whose separation is such that
the Rayleigh criterion is satisfied. For this
reason, we have used a different opera-
tional definition. We define the spectral
line width as follows: The spectral line
width or bandwidth is the width (in nano-
meters) of a monochromatic spectral
line measured at half-intensity with
respect to the adjacent spectral back-
ground. It is important that this line be
"monochromatic," or as free from inter-
ferences as possible. Thus, the spectral
line width is defined here as the full width
at half-maximum (FWHM) intensity of a
monochromatic line.

As noted previously, there are four slits
available for the MD5. Spectra of a low-
pressure mercury lamp were obtained
with an MD5 color version having each of
these slits. A glass bifurcated fiber optic
coupled the lamp housing to the slits. A
piece of ground glass between the lamp
and the input to the fiber optic was used
to attenuate and diffuse the light. Line
width measurements are summarized in
Table II.

From the table it is clear that the line
widths obtained for 50-μm slits are nearly
the same as those obtained for 100-μm
slits. For the color version of the MD5,
the spectral bandwidth is 2.73 nm/diode.
Therefore, the most intense portion of a
monochromatic line image occupies ~3
diodes. If there were no aberrations of
the slit images, the image of a 100-μm
slit should occupy ~2 diodes since the
pixel width is 50 μm. It appears that aber-
rations thus limit the bandwidth to
~10 nm, and that the effective image
width is ~150 μm for either a 50-μm
or 100-μm slit. The maximum MD5
spectrometer f-number is f/2.0. If the f-
number were made larger, the image

quality should improve because of re-
duced astigmatism, with a corresponding
reduction in line width. The limiting im-
age width would then be the pixel width,
which for this detector is 50 μm. If a
50-μm image were obtained, the image
could occupy at most 2 pixels, or an ap-
parent image width of 100 μm. The corre-
sponding minimum line width would thus
be ~5.5 nm.

Line widths were measured in a similar
fashion for the UV, clinical, and near-IR
versions of the MD5. For the UV and clin-
ical versions, a mercury lamp was used,
whereas an argon lamp was used for the
near-IR version. The MD5 slit in all cases
was 50 μm × 2.5 mm. A bifurcated fiber
optic — optical quartz for the UV and
glass for the visible and near-IR — cou-
pled the source to the MD5. The ferrules
of the fiber optic were positioned ~5 mm
from the slits. The line width measure-
ments are summarized in Table II. The
estimated uncertainties in the line width
measurements range from ±0.5 nm for
the UV version to ± 1.5 nm for the near-IR
version.

WAVELENGTH RANGES

To determine the wavelength ranges of
the MD5, a mercury or argon lamp was
coupled to the slits using a glass or
quartz bifurcated fiber optic. The MD5
slits were 50 μm × 2.5 mm. The MD5
was equipped with the appropriate glass
filters and detector described previously.

Wavelength calibration was performed
using linear regression. The required in-
put for each line is the wavelength and
the location of the peak in terms of diode
number. Although the peak diode num-
ber can be estimated to within ±0.5 diode
from an inspection of the saved spectral
data file, better accuracy was achieved by
exporting the data file into LabCalc. a

feature of LabCalc, which was actually de-
signed for chromatography, can be used
to obtain peak maxima to approximately
±0.1 diode. The wavelength ranges using
the calibration data are summarized in
Table III.

The spectral ranges given in Table III
do not include the possible effect of the
filter glasses used in the MD5. The calcu-
lated transmission of the glasses used in
the clinical and color versions are ~50%
at the shortest wavelengths given in
Table III. The filter used in the near-IR
version, however, has ~5% transmission
at 580 nm, and ~50% at 590 nm.

STRAY LIGHT

Stray light was measured using glass fil-
ters, which are essentially opaque at the
wavelength of interest, but transmit at
longer wavelengths. The 50-mm square
× 3-mm thick filters selected were from

Table I. Lines of the low-pressure mer-
cury (Hg) and argon (Ar) lamps useful
for MD5 wavelength calibration.

Spectral region	Lamp	Wavelength (nm)
UV	Hg	253.7, 296.7, 312.9 (312.6/313.2), 334.2
Visible	Hg	404.7, 435.8, 546.1, 578.0 (577.0/579.1)
Near-IR	Ar	696.5, 763.5, 912.3, 965.8

Table II. Mean spectral line widths and
standard deviations of atomic lines
measured with the MD5.

Version	Slit	Mean width (nm)	SD (nm)
Color	50 μm × 1 mm	8.5	2.1
	50 μm × 2.5 mm	7.9	1.1
	100 μm × 1 mm	9.1	2.0
	100 μm × 2.5 mm	8.4	1.1
Clinical	50 μm × 2.5 mm	6.9	1.3
UV	50 μm × 2.5 mm	2.9	0.7
Near-IR	50 μm × 2.5 mm	13.6	4.6

Lines measured:
Color: Hg 404.7, 435.8, 546.1, 578 (unresolved doublet)
Clinical: Hg 365.2 (unresolved triplet), 404.7, 435.8, 546.1, 578.0
UV: Hg 253.7, 296.7, 312.9, 334.2
Near-IR: Ar 696.5, 763.5, 912.3, 965.8

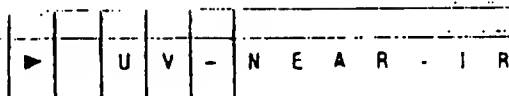**Table III.** Measured wavelength ranges
for the MD5 modules.

Model	Range (nm)	Estimated uncertainty (nm)
UV	190–360	±5
Clinical	330–630	±10
Color	380–730	±10
Near-IR	580–1100	±15

▶ | U | V | - | N | E | A | R | · | I | R

Table IV. Stray light ratios for the color MD5 using tungsten (W), deuterium (D₂), and xenon (Xe) lamps.				
λ (nm)	W	W + KG5 filter	D₂	Xe
400	0.1	0.02	1×10^{-3}	2×10^{-3}
500	0.01	2×10^{-3}	6×10^{-4}	1×10^{-3}
600	6×10^{-3}	4×10^{-4}	5×10^{-4}	1×10^{-3}

A Schott publication (2) giving transmission characteristics was obtained from the manufacturer. Filters used and the measurement wavelengths were: GG475 (405 nm), OGS50 (500 nm), RG645 (600 nm), RG780 (700 nm), and RG1000 (800 nm). All of these filters except RG1000 had an internal transmittance of $<10^{-5}$ at the measurement wavelength: for RG1000 the transmittance was 5×10^{-5}.

Both tungsten-halogen (40-W) and deuterium (30-W) lamps were used for stray light measurements. The lamps were in a common housing that was part of a model 139 Perkin-Elmer (Norwalk, CT) spectrophotometer. The aperture of the lamp housing was imaged onto the single-bundle end of a Dolan-Jenner Industries (Lawrence, MA) glass bifurcated fiberoptic bundle, and the two legs of the fiber optic were attached to an adapter near the MD5 slits.

To measure the stray light, the spectrum of the lamp was obtained without a filter in place. A Schott filter was then installed and the filter spectrum recorded. Finally, light was blocked and a "dark" spectrum was obtained. Data were saved to an ASCII text file and exported to Lab-Calc for manipulation and display. The spectrum of the low-pressure mercury lamp was obtained to establish wavelength calibration. The stray light ratio (SLR) is defined as the ratio of the intensity of the source with a filter installed to the intensity without a filter at the measurement wavelength (dark signals subtracted); the smaller the ratio, the lower the amount of stray light relative to desired light. It should be emphasized that the stray light measured in this manner is total (integrated) stray light at wavelengths longer than the measurement wavelength.

In most instances a similar set of measurements was obtained including a Schott KG5 filter (3-mm thick) with the cut-off filters. This filter removes most of the light beyond ~850 nm. SLRs for the color version of the instrument are given

in Table IV. From Table IV, SLRs using a deuterium lamp are ~10^{-3}: the ratios are about the same with or without a KG5 filter. The SLRs are much greater for a tungsten lamp unless a KG5 filter is used. The improvement in SLRs using the KG5 filter is due to the prevention of most of the near-IR light from entering the instrument. This light can scatter from the grating and other surfaces, thus contributing to stray light. In addition, silicon detectors are particularly sensitive to near-IR light up to ~1100 nm. For these reasons, the use of a KG5 filter or similar near-IR-absorbing filter is recommended when using a tungsten lamp in the visible region.

More recently, stray light was measured for the color MD5 using a 10-W xenon flash lamp (EG&G FX280). These data are included in Table IV. Data shown in this table were obtained without the use of a KG5 filter; however, the KG5 filter further reduces stray light by factors of two to four.

SLRs obtained for the near-IR version with the tungsten lamp were 2×10^{-3} (600 nm), 7×10^{-4} (700 nm), and 4×10^{-4} (800 nm). The measurement uncertainties in the SLRs are quite large due to the very small signal (nearly at the dark level) associated with the filter measurement. These uncertainties range from ~100% in the visible region to ~300% in the near-IR region.

SENSITIVITY
Instrument sensitivity is defined here as the minimum detectable signal (when the signal is three times the noise) of an MD5 color optical module with the EG&G RL0256TBU diode-array detector and electronics. To measure sensitivity, the MD5 spectrometer was mounted on an optical bench having a 40-W tungsten lamp. Two pieces of ground quartz were placed over the exit aperture of the lamp housing for attenuation and improved image uniformity. A quartz lens with an attached iris diaphragm focused the rectan-

gular lamp aperture onto the slit. The iris diameter and lens focal distance were adjusted to give an input f-number of 2.0, thus matching the spectrometer f-number.

Irradiance measurements at specific wavelengths were obtained with four interference filters positioned near the lamp: 420 nm, 521 nm, 525 nm, and 650 nm. The filter bandwidths ranged from ~12 nm to 22 nm. A neutral density filter (density 3.0) was placed in the optical path to further reduce the intensities of light transmitted through the filters.

The MD5 was temporarily removed from the optical bench and in its place was positioned a calibrated silicon detector (Model 818-ST, SN404, Newport, Irvine, CA). The detector surface was positioned at the location of the MD5 slit. The detector size was 10 mm × 10 mm and was therefore much larger than the physical size of the image. The detector photocurrents for each filter were measured using a Keithley (Cleveland, OH) Model 417 picoammeter. Three or four measurements were taken with each filter in place, and then with the light through the filters blocked. The "dark" signals from residual ambient light were subtracted from the filter signals.

After the above measurements were made, the MD5 spectrometer was returned to the optical bench with one slit at the position previously occupied by the Newport detector. The same interference filters (with neutral density filter) were again measured and the data stored to ASCII-format files. These data files, consisting of the signals in A/D counts and diode number, were imported to LabCalc for further analysis and display. Also stored were the background (dark) measurements, which were then subtracted from each filter spectrum.

MINIMUM IRRADIANCE AT SLIT
The average photocurrents for the four filters and the Newport detector responsivities are summarized in Table V. Also included in this table are the measured signal-to-noise ratios (S/Ns) with a neutral density 3.0 (ND3) filter positioned after the interference filters. S/Ns are with dark counts subtracted. Spectral bandwidths of the filters (FWHM intensities) are also given.

The following is a sample calculation of the minimum spectral irradiance at the

Table V. Experimental data for estimating MD5 spectrometer sensitivity. Detector pho-tocurrents are without the ND3 filter in place. The minimum irradiances (S/N = 3) are given in the last column.

Filter (nm)	Detector responsivity (A/W)	Detector current (µA)	Filter bandwidth (nm)	Signal/noise (with ND3)	Minimum Irradiance (pW/cm² nm)
420	0.2295	0.240	21.5	24.6	25
521	0.3167	0.329	12.4	52.4	20
525	0.321	0.770	11.6	132	20
650	0.4128	1.17	13.2	131	21

MD5 slit for the 525-nm filter. The power incident on the Newport detector with the ND3 filter in place is (from Table V):

$$0.770 \times 10^{-6} A \times W/0.321 A \times 10^{-3} =$$
$$2.40 \times 10^{-9} W \qquad [1]$$

Since the image area is 4 mm × 6 mm = 0.24 cm², the calculated spectral irradi-ance is:

$$2.40 \times 10^{-9} W/(0.24 cm^2 \times 11.6 nm) =$$
$$8.62 \times 10^{-10} W/cm^2 nm \qquad [2]$$

The corresponding S/N of the filter band corresponding to this irradiance is 132. For a S/N = 3 (a reasonable esti-mate of detectability) the scaled irradi-ance is 1.96×10^{-11} W/cm² nm, or 19.6 pW/cm² nm. Calculated minimum irradiances at the four wavelengths are given in Table V.

These estimates of sensitivity may be used to determine whether the amount of light available to the instrument will provide adequate signal to noise. This as-sumes one knows the power of the inci-dent source, the fraction of power trans-mitted or reflected by the sample, and losses due to transfer optics. We have used these estimates to predict the instru-ment sensitivity for measurement of qui-nine sulfate fluorescence; agreement with the experimental value was within a fac-tor of two.

APPLICATIONS

Principal applications for dual-beam spec-trometry are transmission (absorption) and reflectance measurements. As an ex-ample of a reflectance measurement, sev-eral colored ceramic tiles were measured using a 10-W xenon flash lamp (EG&G FX280U). The flash lamp was mounted vertically in a stand with two fiberoptic bundles in proximity to the lamp enve-lope. A sampling accessory supported two fiberoptic bundles close to the sam-ple surface. Light from the lamp was con-ducted through the fiberoptic bundle to the sampling accessory, and was directed normal to the sample surface. Light re-flected from the sample surface was col-lected at 45° by the other fiber bundle and carried to the spectrometer slit. There were two such sampling acces-sories, one for the sample (colored) tile and the other for a reference (white) tile. All fiber bundles were optical grade fused silica (Dolan-Jenner Industries).

Figure 5 shows spectra of the xenon lamp obtained in reflectance from a white ceramic tile, for both sample and refer-ence. The vertical axis is in units of A/D counts. An MD5 color version was used for these measurements. The wave-lengths for the two spectra vary from ~380 nm near the center of the array to ~730 nm at the ends of the array (com-pare with the spectrum of the mercury lamp in Figure 4). Figure 6 shows the ra-tio of these same two spectra, with sig-nals interpolated to specific wavelength increments using the wavelength calibra-tion data. The irregular line is the ratio spectrum using the spectra of Figure 5; the irregularities are due to calibration er-rors and small optical differences in the two spectra. This spectrum can be stored and used as a correction factor for subse-quent ratio data. The result of dividing a ratio scan by this stored correction factor gives the nearly straight line in Figure 6.
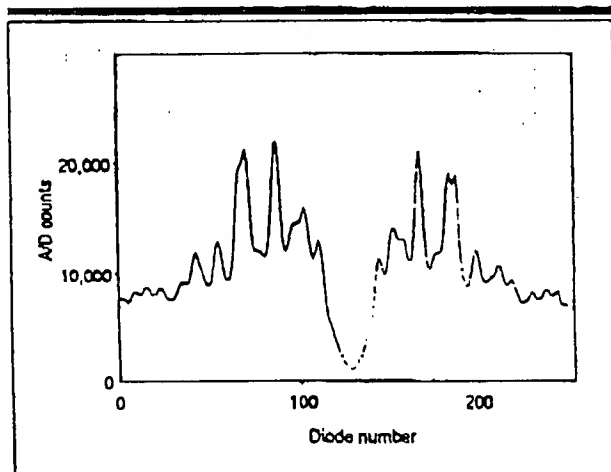
Figure 5. Spectrum of a xenon flash lamp measured in reflectance from a white ceramic tile.
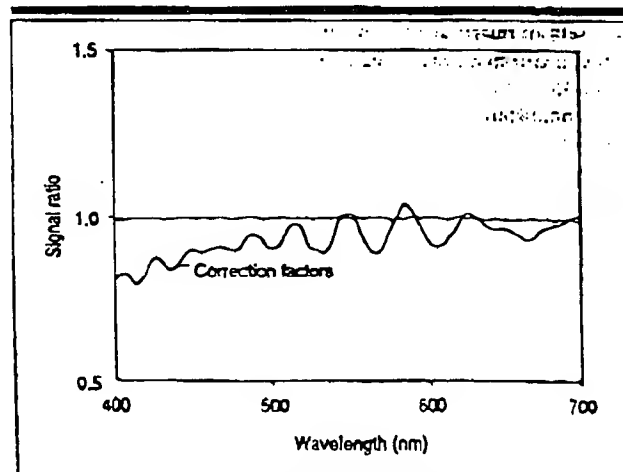
Figure 6. Spectrum of a xenon flash lamp reflected from a white tile in ratio mode. The irregular line is the ratio spectrum using the spectra from Figure 5, which can be used as a correction factor. The straight line results from dividing a ratio scan by this stored correction factor.
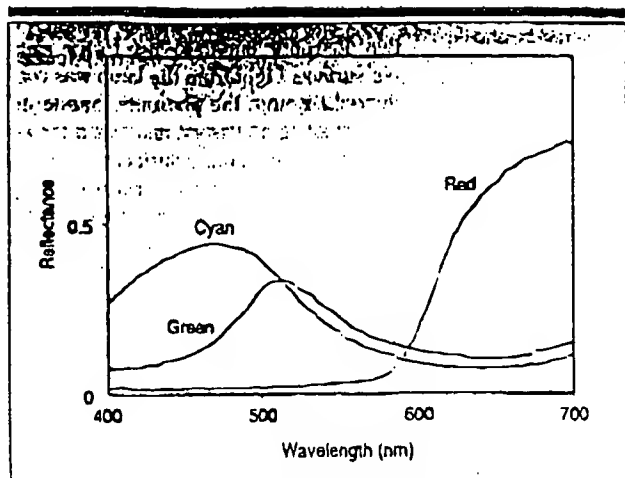
Figure 7. Reflectance spectra of colored ceramic tiles measured relative to a white tile.
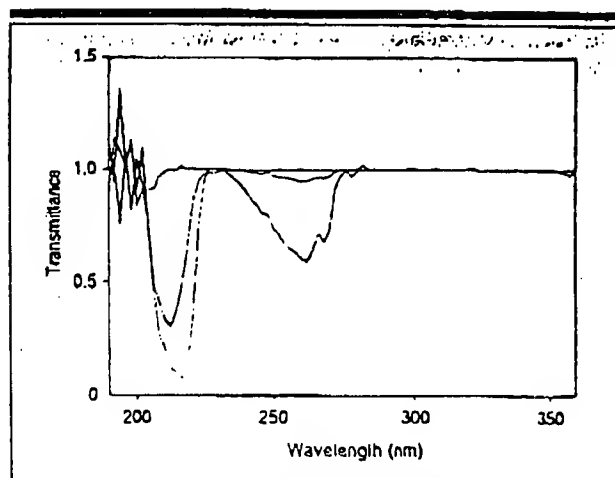

Figure 8. Transmission spectra of toluene in methanol v. methanol (concentrations 0, 10, and 100 ppm) using a xenon flash lamp.

Figure 7 shows the spectra of several colored tiles, using the stored correction factor as a divisor. All spectra were measured relative to a white tile. The spectra show the expected higher reflectance associated with the color of the tile; for example, the peak reflectance near 700 nm is for the red tile. All data were obtained with a single flash of the xenon flash lamp, for which the pulse-to-pulse variation was 0.5-1% root mean square (RMS).

Transmission measurements are more appropriate if the sample is transparent in the wavelength region of interest. A dual-beam measurement fixture designed for use with a xenon flash lamp consisted of two aluminized plane mirrors and two sets of quartz lenses to direct light through two fused silica cells (1-cm path length).

Transmittance spectra of toluene in methanol using the UV version of the MD5 is shown in Figure 8. The main features of the spectra agree with a published spectra in hexane (3); the published spectra shows three absorption maxima at ~189, 208, and 262 nm. The spectra obtained here is distorted at short wavelengths because of solvent absorption and other optical losses below ~225 nm. The baseline RMS noise for single flashes of the lamp is about 1%. Data from multiple flashes could be averaged for lower noise.

For the above examples, the sample was measured relative to a white surface or pure solvent. However, with a dual-beam spectrometer the reference material can be whatever is relevant to the mea-

surement. For example, for a color measurement the reference could be a sample of the material with "acceptable" color characteristics. Similarly, the transmission of an organic liquid or polymer film could be referenced to that of a similar material having the desired properties.
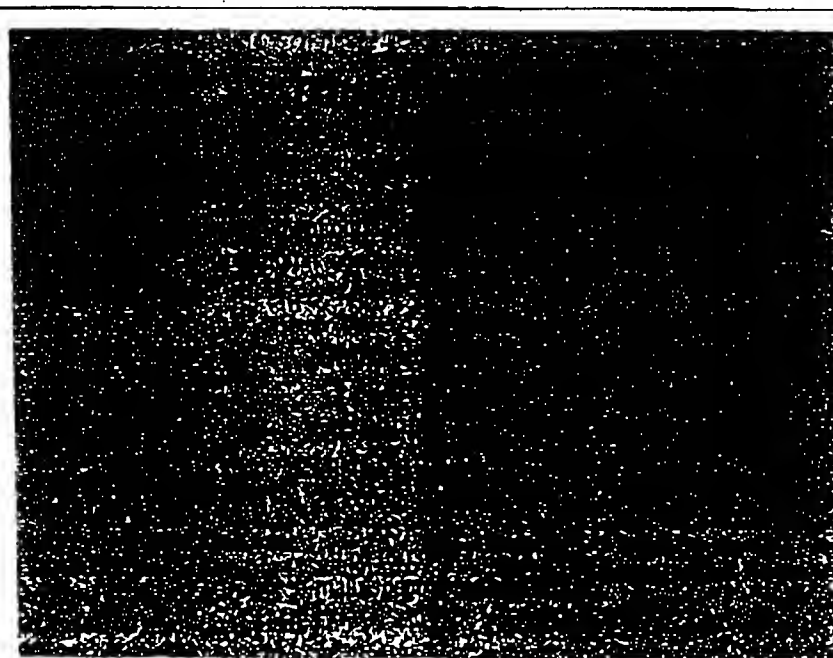
ACKNOWLEDGMENTS

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